# 論文 CHLORIDE ION INGRESSION THROUGH AND AROUND THE CRACK IN REINFORCED CONCRETE STRUCTURES

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**ABSTRACT:** This study was carried out in order to observe the penetration profile of the chloride ions through cracks in reinforced concrete structures. Concentration and penetration depth profile of Cl<sup>-</sup> ions might be useful information to consider degradation of life span of structures due to localized corrosion where a crack exists. EPMA and Colorimetric tests were conducted on specimens exposed to NaCl solution under different exposure conditions. The increase of w/c leads obvious dilation on ingression rate of Cl<sup>-</sup> ions not only from exposed surface but also around the crack. In general, the penetration depth around crack is higher than that from exposed surface except for those with very low w/c of 0.25.

**KEYWORDS:** EPMA, colorimetric test, crack, crack width, chloride ions penetration, chloride ions concentration, penetration depth

## **1. INTRODUCTION**

Untimely, requirement of rehabilitation of bridges, roads, marine structures and the likes due to chloride-induced corrosion is emerging as a major problem to be solved. Due to the same reason, a considerable number of structures become inadequacy in functionalities and no longer are serving satisfactorily. Service life of the reinforced concrete structure could be drastically shortened if the structure has cracks, which can rapidly transport the harmful gas and liquid to reinforced steel. The estimation of life span of reinforced concrete structures having cracks may be influenced by the characteristics of cracks such as crack width, crack length and so on in additional to the concrete properties and exposure conditions.

Most of the previous research works were done as modeling of diffusion of chloride ions through an uncracked concrete based on the Fick's second law, where diffusion mechanism was the main concern. However, in practical, it is very usual to have some cracks in the concrete structures situated in the chloride ion environment. In that case, the transportation of chloride ions by water or moisture movement could be as fast as only taking few hours to reach the steel while penetration of the ions in the uncracked concrete taking pretty long time.

Critical chloride ion concentrations for different grade and types of steel bars were defined in terms of probability of corrosion initiation as a function of the free chloride ion concentration. For ordinary steel, the average value of 0.4% of free chloride ions to cement weight with standard deviation of 0.15% [1]. The application of which could be found as threshold limit in some literatures [2]. A wide range of values of the critical chloride ion concentration for ordinary steel have been determined [3]. The frequently used ratio of 0.4% of total chloride ions to cement weight is often overly pessimistic with regard to initiation time of corrosion for in situ conditions.

The inward movement of Cl<sup>-</sup> ion into the cracked concrete could be through the capillary system, through hydration products like C-S-H gel and cracks in paste structure. However, the movement through C-S-H gel is much slower compared to others and is negligible for all practical purpose. The pore solution contains chemical ions from dissolved solid materials from paste system such as hydroxyl ions (OH<sup>-</sup>), alkali ions such as K<sup>+</sup> and Na<sup>+</sup> as well as calcium, aluminates, sulfate etc. [4].

A study was carried out on six series of small reinforced concrete beams (prisms) with variations of water to cement ratio (w/c), single and multi cracks, exposed direction, crack width, NaCl concentration, and cover thickness. As a main parameter, specimens with w/c of 0.45, crack width of 0.2 mm, NaCl concentration of 8% and cover thickness of 2.5 cm were used.

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# 2. EXPERIMENTAL PROGRAM

# 2.1 PREPARATION OF SPECIMENS AND MIX PROPORTIONS

Six series with 11 types of specimens were prepared for this study as shown in Table 3. Beam (Prism) specimens of 10 x 10 x 40 cm were adopted with 2 x  $\Phi$ 10 mm plain bar reinforcements for single crack specimens and deformed bars for multi cracks specimens at the tension side.  $\Phi$ 10 x 20 cm cylinders were used for compressive strength testing.

Concrete ingredients used were Type I Portland cement with  $5\sim12.3$  mm crushed stone, fine aggregate, tap water and superplasticizer for water to cement ratio of 0.25. The superplasticizer (SP) used here was Rheobuild 8N, with specific gravity of 1.05 and Cl<sup>-</sup> content less than 0.01%. The composition and property of cement used is shown in Table 1.

**Table 1. Composition and Property of Cement** 

Specific Gravity	3.16		
Specific surface	$3260 \text{ cm}^2/\text{g}$		
area	5200 cm /g		
Setting time			
Initial set (h:min)	2:15		
Final set (h:min)	3:40		
Soundness	Good		
MgO	1.44%		
SO <sub>3</sub>	2.02%		
IG loss	1.65%		
Alkali content	0.54%		
Cl content	0.012%		

The mix proportion was referred to the Concrete Manual [5]. The mix proportion, density and 28 days compressive strength of concrete were expressed in Table 2. During the first 28 days of concrete age, the specimens were sealed in plastic bag. After that, loading was applied to get required crack width. Crack width was measured by using PI gauges while loading and crack gauge after released of loading. Visible crack length ranges from 6 to 9 cm. Three point bending test was applied to the single cracked specimens and four point bending test to multi cracked (mostly two cracks) specimens. The crack width of multi cracked specimens could not be controlled to be uniform width. The crack width of 2 cracks of multi-cracked specimens in this study was 0.1 and 0.2 mm.

The specimens were coated with epoxy to prevent penetration of Cl<sup>-</sup> ion from the unintentional sides. Therefore, coating was done

depending upon the direction of flow of NaCl solution. After all preparations, the specimens were kept in the control room of 20 °C and RH of 60% pre-curing and waiting for exposure to NaCl solution.

Sr.No	w/c	Cement (Kg/m³)	Water (Kg/m <sup>3</sup> )	Sand (Kg/m <sup>3</sup> )	Coarse Agg. (Kg/m <sup>3</sup> )	Agg Vol. (%)	C Strength (Mpa)	SP, Rehobuild	Dry Density (Kg/m <sup>3</sup> )
1	0.25	720	180.0	614.40	880.50	57.1	81.04	0.80%	2356
2	0.45	424	190.8	768.00	941.60	67.3	45.04	-	2284
3	0.65	277	180.0	911.40	947.00	71.2	27.86	-	2238

Table 2. Mix Proportion and Property of Concrete

The experimental set up was started at 3 months of concrete age in the control environment of 20 °C and RH of 60% room. The specimens were laid in the solution trays of specified concentration for exposure time of 7 days and 1 month (All series for 7-days exposure whilst only 5 specimens for 1 month exposure were carried out as shown in Table 3).

From the remark of Table 3, the 1 direction means that the specimens were exposed to Cl<sup>-</sup> ions from the bottom surface and we expect that the vertical flow of NaCl solution parallel to the crack direction will mainly take place. The 2 direction means that the solution can be penetrated through the bottom and one of the side surfaces of the beam specimen. For each flow direction, the coating was applied accordingly to unexposed surfaces by using primary, putty and epoxy as final coat. Clear cover thickness means that the distance between the concrete surface of the tension side of beam and the reinforced steel surface. Therefore, the cover thicknesses applied in this study are 3 and 5 cm respectively to center of the steel.

As a matter of actual fact, the crack widths mentioned were initial crack widths before exposure and they reduced by time, which could not be controlled in this set up of experiment. The crack width was controlled in the other experimental set up by using torque wrench through out the exposure time and the results will be presented in separate paper. The single and multi crack series is to observe the effect of adjacent crack of beam specimens those having two or more cracks.

No.	Mix ID	wc	Cracks	Crack width (mm)	Cl- concentr- ation (%)	Clear Cover thickness (cm)	Crack Length 7days exposed (cm)	Crack Length 1 month exposed (cm)	Remark	
Series	s 1) Wa	ter to Ce	ment Ratio	(w/c)						
1	А	0.45	Single	0.2	8%	2.5	7.85	8.30	1 direction	
2	в	0.25	Single	0.2	8%	2.5	7.60	6.75	"	
3	С	0.65	Single	0.2	8%	2.5	8.10	5.65	"	
Series	s 2) Sinț	<b>gle and</b> I	Multi Crack	<u>s</u>						
1	А	0.45	Single	0.2	8%	2.5	7.85	8.30	1 direction	
4-1	D-1	0.45	Multi	0.1	8%	2.5	5.70	-	"	
4-2	D-2	0.45	Multi	0.2	8%	2.5	10.00	-	"	
Series 3) Exposure Direction										
1	А	0.45	Single	0.2	8%	2.5	7.85	8.30	1 direction	
5	Е	0.45	Single	0.2	8%	2.5	7.45	-	2 direction	
Series	54) Gra	ck Width	<u>i</u>							
6	F	0.45	Single	0.1	8%	2.5	6.35	-	1 direction	
1	А	0.45	Single	0.2	8%	2.5	7.85	8.30	"	
7	G	0.45	Single	0.3	8%	2.5	8.55	-	"	
8	Н	0.45	Single	0.5	8%	2.5	8.75	-	"	
Series	5) Na	a Conce	entration							
9	Ι	0.45	Single	0.2	3%	2.5	7.90	6.90	1 direction	
10	J	0.45	Single	0.2	5%	2.5	8.45	-	"	
1	А	0.45	Single	0.2	8%	2.5	7.85	8.30	"	
Series	5 6) Cov	ver Thick	aness							
11	Κ	0.45	Single	0.2	8%	4.5	8.05	7.35	1 direction	
1	А	0.45	Single	0.2	8%	2.5	7.85	8.30	"	
	10	¢ ¢ ¢	40 8 cm		Cl lons Exposed PMA specimen	Crack Plane				

Fig.2 Location of EPMA Specimen in Small RC Beam

#### **3. RESULT AND DISCUSSION**

Mix ID Period of Exposure

#### Fig.1 Nomenclature of Specimen ID

#### **2.2 TESTING DETAILS**

The tests performed on the exposed specimens include Electron Probe Micro Analysis (EPMA) for Cl<sup>-</sup> ions concentration and penetration depth profile. Colorimetric tests with 0.1 Mol/l Silver Nitrate Solution for checking of penetration depth of Cl<sup>-</sup> and 1.0 weight/volume % ions Phenolphthalein Ethanol (90) solution (for PH> 7.8) for carbonation depth were done on separate adjacent cut specimens since spraying could not be carried out on the EPMA tested specimens.

Without using water or oil to avoid the disturbance of Cl- ions distribution in the specimen, they were cut by using two different dry diamond blade cutters. The cut location inside the beam was shown in Fig.2. The sizes of the specimens for EPMA were 7.6 cm (length) x 7.6 cm (width) x 1.8 cm (thick). From which, the total digital data size of  $\sim 400 \text{ x} 400$  numbers were resulted for each of elements conducted and they were used to analyze. The concentration profile of Na<sub>2</sub>O, K<sub>2</sub>O and SO<sub>3</sub> were also detected by EPMA to get supporting data on the movement of Cl<sup>-</sup> ions and carbonation if any.

Once the bottom surface of beams for 1 direction exposure were started expose to NaCl solution, the bulk movement of solution containing Cl<sup>-</sup> ions take place along the crack and lead to deep penetration till above the crack tip within very short time. The flow inside crack took place within a minute and reached to crack tip. Due to continuous supply of solution, the moisture flow took place within 3 hours to reach to the top of the specimen of 10 cm thickness. Although the visible crack length from side of specimens were in range of ~ 6-9 cm as shown in Table 3, the NaCl solution was penetrated till top of the specimens and the spreading on the top of the most specimens was observed except all 0.25 w/c, 0.1 mm crack width and some of 4.5 cm cover thickness specimens after 3 days of exposure.

While the capillary suction flow of bulk movement of solution within the crack is taking place during exposure, the secondary movement of moisture containing Cl<sup>-</sup> ions around the crack that is in perpendicular direction to the crack also takes place.

Penetration from surface

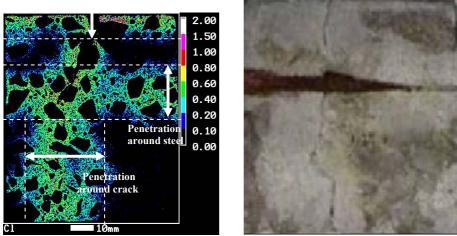


Photo.1 EPMA and Colorimetric Test Images of Cl<sup>-</sup> Ions Distribution for A-7D Specimen

A horizontal flow of Cl<sup>-</sup> ions along the steel when occurred the penetrated ions in the crack reached near to the level of steel. As the interface between the steel and concrete possesses weaker nature of structure, the flow in that direction is considerably fast as shown in Photo.1. An exceptional case for very low water cement ratio of 0.25 mixes showed no flowing along the steel due to the dense structure of concrete.

# **3.1 CARBONATION**

According to the colorimetric test with Phenolphthalein Ethanol solution, the 7 days exposed specimens showed no carbonations at all. However, most of the 1 month exposed specimens except 0.25 w/c specimens, showed a very slight carbonation along the crack. Due to that fact, although some minor changes on  $K_2O$  and  $SO_3$  distributions from EPMA results were expected, which did not exhibited.

## **3.2 PENETRATION DEPTH OF CHLORIDE ION**

For EPMA test, the penetration depths were obtained from the average value of direct measurement from the grid lines on the image files. The clear profile can be seen for the concentration of higher than 0.1% by weight of concrete Photo.1. For colorimetric test, measurements were carried out after 3 days of Silver Nitrate solution was sprayed on freshly cut specimens.

Generally, it is found that the penetration depth around the crack surface is slightly higher than twice of that from the exposed surface except low w/c of 0.25 mixes. It seems that the penetration from the surface of the crack is similar in nature to the one penetrated from the exposed surface and the reason of slightly higher might be due to presence of broken open pores and microcracks along the crack surface.

Increased in w/c, NaCl solution concentrations and crack widths could penetrate deeper especially for longer exposure time of 1 month Fig.3, 4 and 5. No significant differences on penetration depth were observed for the other series.

The penetration depth around steel of some inspected specimens showed about twice of the diameter of the steel bars used for both 7 days and 1month exposed specimens.

The comparisons are made on the depths from EPMA and colorimetric tests for some specimens since not all the colorimetric tested specimens showed clear profile. The match able results with only small differences were found for those mixes as shown in Fig.6. Therefore, although the colorimetric test could not present the actual results for all cases, it may be useful for preliminary viewing stages.

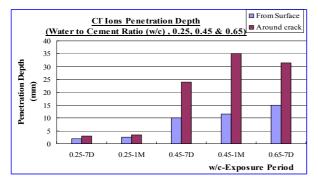


Fig.3 Cl<sup>-</sup> Ions Penetration Depth of w/c Series

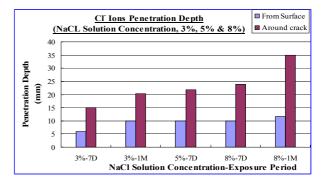
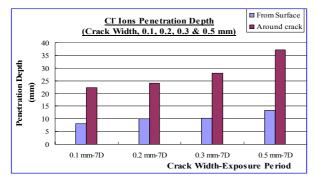


Fig.4 Cl<sup>-</sup> Ions Penetration Depth of NaCl Concentration Series



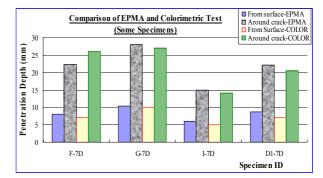
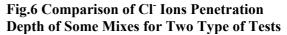


Fig.5 Cl<sup>-</sup> Ions Penetration Depth of Crack Width Series



# 3.3 CONCENTRATION PROFILE OF CI ION, SO<sub>3</sub>, K<sub>2</sub>O AND Na<sub>2</sub>O

All the concentration data presented here are in percent weight of concrete which resulted from the EPMA test. The concentration value at a particular depth means average concentration of 2 mm depths each. As expected, from the w/c series and NaCl solution concentration series, a clear trend is found that the higher the w/c ratio and NaCl solution concentration, the higher concentration of  $Cl^{-}$  ions over the depth of specimen due to existence of cracks Fig.7, 8 and 9.

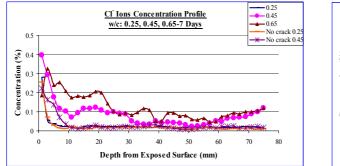
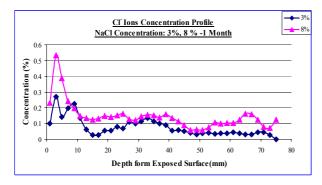


Fig.7 Cl<sup>-</sup> Ions Concentration Profile of w/c Series



## **Fig.9 Cl<sup>-</sup> Ions Concentration Profile of NaCl Solution Concentration Series-1M**

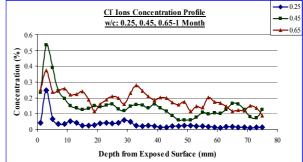


Fig.8 Cl<sup>-</sup> Ions Concentration Profile of w/c Series

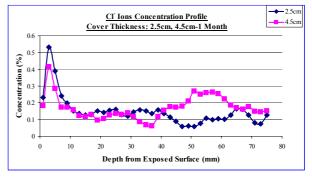


Fig.10 Cl<sup>-</sup> Ions Concentration Profile of Cover Thickness Series-1M

However, the cover thickness series showed a crossing curve with higher concentration near the location of steel for each mixes Fig.10. Occurrence of some damages while loading stage around the steel bars may increase the concentration around that area. Except 0.5 mm crack width specimen, the crack width series showed more or less similar distribution of concentration over depth regardless of crack width. This might be due to the smooth movement of Cl<sup>-</sup> ions along the crack since the solution was supplied continuously. The effect of crack width might be clearer in case of wet and dry supply cycles and long term exposure. Similarly, the Cl<sup>-</sup> ions concentration distribution result after 7 days exposed of 2 direction exposure specimen showed only slightly higher than that of 1 directional specimen over the depth due to very short exposure time.

The Cl<sup>-</sup> ions concentration around the steel of 7 specimens such as H-7D, D2-7D, B-1M, A-1M, C-1M, I-1M and K-1M were studied. It was found that, concentrations around the steel were considerably high except for those with low w/c of 0.25 specimens, which showed no ions movement along the steel.

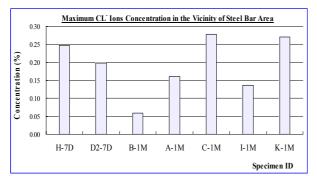


Fig.11 Max. Cl<sup>-</sup> Ions Concentration Around Steel

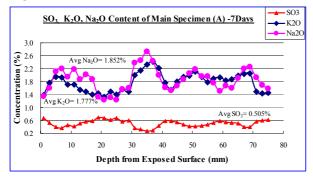


Fig. 13 Concentration of SO<sub>3</sub>, K<sub>2</sub>O, Na<sub>2</sub>O

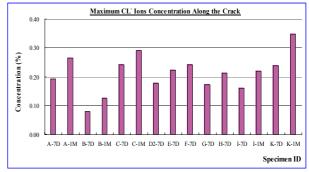


Fig.12 Cl<sup>-</sup> Ions Concentration Along Crack

From Fig.11, although the maximum concentration of Cl<sup>-</sup> ions around steel bar of some mixes exceeded the optimum limit of 0.4% of free chloride by weight of cement (which is equivalent to 0.198% for 0.45 w/c and 0.132% for 0.65 w/c by weight of concrete in this study, by assuming free to bound chloride ratio of 0.6), the corrosion initiation was not seen. It might be due to not enough supply of oxygen to the steel area and short exposure time. From Fig.12, the maximum Cl<sup>-</sup> ion concentration along crack which is average value within 2 mm distance around the crack can be observed. The

concentration of SO<sub>3</sub>, K<sub>2</sub>O and Na<sub>2</sub>O were not effected by existence of cracks on specimens. The origin of SO<sub>3</sub> is from the cement. Although cement includes some alkali contents, K<sub>2</sub>O and Na<sub>2</sub>O mainly are found from aggregates. The fluctuation of the curves showed the aggregate and cement paste intensity along the depth of specimen and the average values of content are almost same for same w/c ratio specimens Fig.13.

# 4. CONCLUSION

The concrete specimens having cracks showed rapid penetration of Cl<sup>-</sup> ions which reached to steel and the penetration along steel also occurred. Very low water to cement ratio of 0.25 specimens showed much lower of penetration depth from surface and around crack, concentration around and along crack, no penetration along steel compared to other specimens. The increase of w/c leads obvious dilation on ingression rate of Cl<sup>-</sup> ions not only from exposed surface but also around the crack. In general, the penetration depth around crack is slightly higher than that from exposed surface except for those with very low w/c of 0.25. From this study, rapid and free movement of Cl<sup>-</sup> ions along with the bulk solution movement through the crack and within the concrete can be occurred when the absorption and/or capillary suction of concrete take place. This was a dominant fact than the diffusion mechanism and should not be ignored for real structures. There might have a critical limit of free ion movement due to flow of bulk solution and followed by diffusion mechanism after steady stage of flow.

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